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Received for review November 13, 1978. Accepted January 26, 1979. Supported in part by the National Institutes of Health (Grant No. 5 P01 ES00049 to J.E.C.) and the Deutsche Forschungsgemeinschaft (grant to I.S.).

Crystal and Molecular Structure of Organophosphorus Insecticides. 12. Dowco 214

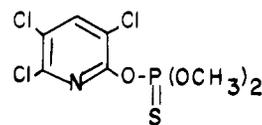
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The crystal and molecular structure of Dowco 214 [*O,O*-dimethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] has been determined by single crystal X-ray techniques. It crystallizes in space group $P\bar{1}$ with $a = 11.598$ (2), $b = 13.619$ (3), $c = 8.281$ (1) Å, $\alpha = 94.65$ (1), $\beta = 94.87$ (2), and $\gamma = 79.97$ (2)° with four molecules per unit cell (two per asymmetric unit). A modified Patterson superposition procedure yielded an initial model and subsequent least-squares refinement based on 3810 observed reflections ($|F_o| > 3\sigma_{F_o}$) gave a final residual index of $R = 0.078$. The geometry around the phosphorus is distorted tetrahedral with the P-O bond to the aryl group being somewhat elongated relative to the others, averaging 1.616 (4) Å vs. 1.560 (4) and 1.547 (4) Å. Charge densities as determined by CNDO methods are also presented, along with appropriate distances between positively charged centers.

Structural studies of various organophosphorus (OP) insecticides, with similar formulations but widely differing activities/toxicities, have been undertaken in this laboratory (Baughman and Jacobson, 1975, 1976, 1977, 1978; Baughman et al., 1978a,b; Gifkins and Jacobson, 1976; Rohrbaugh and Jacobson, 1976, 1977, 1978) via single-crystal X-ray diffraction techniques. These studies are part of a program to generate the necessary data base to correlate toxicity of insecticides, particularly of the organophosphorus type, and their structural and electronic features through generation of a body of precise structural parameters. Accurate structural determination of the relatively small OP insecticide molecules allows inferences to be drawn concerning the three-dimensional structure of the active sites on the complex acetylcholinesterase (AChE) molecule. As has been previously discussed (O'Brien, 1960; Fukuto and Metcalf, 1956; Fukuto, 1971; Hansch and Deutsch, 1966; Canepa et al., 1966), the effectiveness of the insecticide appears to depend on a favorable combination of gross topological features, relative charge densities on the sites that bond to the enzyme, and the esteratic-anionic site separations within a range that best accommodate the various AChE enzymes. It is hoped that such structural information will aid in the construction of more specific insecticides conforming to the most favorable configuration to interact with the target AChE molecule.

Among the crystal structures recently completed in this laboratory have been that of chlorpyrifos and its methyl oxon homologue, fospirate (the fourth and fifth references cited above) with LD_{50} 's of 163 and 869 mg/kg, respectively (Osborne, 1976). Continuing in this vein, we decided to carry out a crystal structure analysis of *O,O*-dimethyl

O-(3,5,6-trichloro-2-pyridyl) phosphorothioate, hereafter referred to as Dowco 214, the methyl homologue of chlorpyrifos. It has a much lower mammalian toxicity



($LD_{50} = 1500$ mg/kg; Eto, 1974) than either chlorpyrifos or fospirate and yet is more effective against adult mosquitos.

EXPERIMENTAL SECTION

Crystal Data. Samples of Dowco 214 were kindly supplied by D. W. Osborne of the Dow Chemical Co. A rectangular crystal of approximate dimensions $0.4 \times 0.4 \times 0.6$ mm was mounted on the end of a glass fiber with Elmers Glue-All and attached to a standard goniometer head. Three preliminary ω -oscillation photographs, taken at various χ and ϕ settings on a four-circle diffractometer, provided the coordinates of 11 independent reflections which were input into an automatic indexing program (Jacobson, 1976). The resulting reduced cell and reduced cell scalars indicated triclinic symmetry. Observed layer line spacings on subsequent axial ω -oscillation photographs were equal within experimental error to those predicted by the indexing program.

Lattice constants were obtained by a least-squares refinement of the precise $\pm 2\theta$ ($|2\theta| > 25^\circ$) measurements of 25 strong independent reflections using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.70954$), yielding $a = 11.598$ (2) Å, $b = 13.619$ (3) Å, $c = 8.281$ (1) Å, $\alpha = 94.65$ (1)°, $\beta = 94.87$ (2)°, and $\gamma = 79.97$ (2)°.

Collection and Reduction of X-Ray Intensity Data. Data were collected at 27 °C on an automated four-circle diffractometer described previously (Rohrbaugh and Jacobson, 1974). All data within a 2θ sphere of 50° (5356

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Table I. Final Atomic Positional^a Parameters for Dowco 214

atom	x	y	z
Molecule A			
Cl(1)	1.0656 (1)	0.4265 (1)	0.1637 (2)
Cl(2)	1.1834 (1)	0.3299 (1)	0.7801 (2)
Cl(3)	0.9213 (2)	0.2921 (1)	0.7956 (2)
S	0.6263 (1)	0.4695 (1)	0.3827 (2)
P	0.7036 (1)	0.3736 (1)	0.2318 (2)
O(1)	0.8434 (3)	0.3706 (3)	0.2271 (4)
O(2)	0.6683 (4)	0.3842 (3)	0.0474 (5)
O(3)	0.6883 (4)	0.2647 (3)	0.2549 (5)
N	0.8914 (4)	0.3357 (3)	0.4940 (5)
C(1)	0.9224 (4)	0.3647 (4)	0.3596 (6)
C(2)	1.0329 (5)	0.3874 (4)	0.3427 (6)
C(3)	1.1137 (5)	0.3780 (4)	0.4737 (7)
C(4)	1.0827 (5)	0.3457 (4)	0.6169 (7)
C(5)	0.9689 (5)	0.3270 (4)	0.6215 (7)
C(6)	0.6663 (7)	0.4772 (5)	-0.0306 (8)
C(7)	0.7393 (7)	0.1787 (5)	0.1452 (9)
H	1.1992	0.3942	0.4657
Molecule B			
Cl(1)	0.3812 (2)	0.2679 (2)	0.1610 (2)
Cl(2)	0.5310 (2)	0.2680 (1)	0.7926 (2)
Cl(3)	0.4263 (2)	0.0680 (2)	0.8075 (2)
S	0.0677 (2)	0.1074 (2)	0.3619 (3)
P	0.1869 (1)	0.0312 (1)	0.2394 (2)
O(1)	0.2987 (4)	0.0858 (4)	0.2301 (5)
O(2)	0.1610 (4)	0.0099 (3)	0.0529 (5)
O(3)	0.2362 (4)	-0.0763 (3)	0.2844 (6)
N	0.3637 (5)	0.0856 (4)	0.5016 (6)
C(1)	0.3532 (5)	0.1288 (5)	0.3636 (7)
C(2)	0.3983 (5)	0.2157 (5)	0.3442 (7)
C(3)	0.4540 (5)	0.2575 (4)	0.4776 (7)
C(4)	0.4630 (5)	0.2142 (4)	0.6240 (7)
C(5)	0.4171 (5)	0.1275 (5)	0.6290 (7)
C(6)	0.1095 (7)	0.0904 (6)	-0.0504 (10)
C(7)	0.2310 (7)	-0.1122 (6)	0.4453 (9)
H	0.4884	0.3244	0.4685

^a The positional parameters for all atoms are represented in fractional unit cell coordinates. Positions for methyl hydrogens are not given. ^b In this and succeeding tables, estimated standard deviations are given in parentheses for the least significant figures and include the error in the lattice constants. A difference of more than three standard deviations is considered statistically significant. No standard deviation is given for the unrefined hydrogens.

reflections) in the hkl , $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ octants were measured using an ω -step scan technique.

As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 75 reflections. These standard reflections were not observed to vary significantly throughout the data collection period. A Howells, Phillips, and Rogers (1950) test indicated a center of symmetry and the space group was thus assumed to be $P1$.

The intensity data were corrected for Lorentz and polarization effects but, since $\mu = 9.87 \text{ cm}^{-1}$, absorption corrections were not deemed necessary (maximum and minimum transmission factors were 0.66 and 0.54, respectively). The variance in each intensity was calculated by

$$\sigma^2 = C_T + k_t C_B + (0.03C_T)^2 + (0.03C_B)^2$$

where C_T and C_B represent the total and background counts, k_t is a counting time constant, and the factor of 0.03 represents an estimate of nonstatistical errors. The estimated deviations were calculated by the finite difference method (Lawton and Jacobson, 1968). Equivalent data were averaged and 3810 reflections with $|F_o| > 3.0\sigma(F_o)$ were deemed observed and retained for use in subsequent structure analysis and refinement steps.

Table II. Selected Interatomic Distances (Å) for Dowco 214

	Molecule A	Molecule B
S-P	1.894 (2)	1.893 (2)
P-O(2)	1.559 (4)	1.561 (4)
O(2)-C(6)	1.462 (7)	1.458 (8)
P-O(3)	1.553 (4)	1.540 (5)
O(3)-C(7)	1.492 (8)	1.467 (8)
P-O(1)	1.618 (4)	1.613 (4)
O(1)-C(1)	1.367 (6)	1.367 (7)
C(1)-C(2)	1.390 (7)	1.401 (9)
C(2)-C(3)	1.371 (7)	1.366 (8)
C(3)-C(4)	1.393 (8)	1.379 (8)
C(4)-C(5)	1.392 (8)	1.383 (8)
C(5)-N	1.325 (7)	1.317 (7)
N-C(1)	1.309 (7)	1.315 (8)
C(2)-Cl(1)	1.708 (5)	1.708 (6)
C(3)-H	1.062 (4)	1.066 (5)
C(4)-Cl(2)	1.711 (5)	1.719 (6)
C(5)-Cl(3)	1.717 (6)	1.730 (6)
P-C(3)	5.010 (5)	4.929 (6)
P-C(4)	5.185 (6)	5.136 (6)
P-C(5)	4.271 (6)	4.281 (6)
P-H	5.954 (2)	5.855 (2)
C(6)-S	3.504 (7)	3.472 (9)
C(7)-S	4.318 (7)	3.339 (8)
N-C(6)	5.203 (8)	5.223 (9)
N-C(7)	3.934 (8)	3.311 (9)

SOLUTION AND REFINEMENT

The presence of four molecules per unit cell (as deduced from density considerations) in the space group $P1$ meant that the structural parameters for two molecules per asymmetric unit had to be determined. Conventional Patterson and direct method procedures (Main et al., 1971) were tried but failed to yield any reasonable solution. Therefore, we felt this would be a good test case for our recently developed Patterson superposition method which involves the use of two multiple vector peaks to define a structural parallelogram (Jacobson and Beckman, 1979). This method readily revealed the positions of the nearly tetrahedral thiophosphate groups and the bridging ring carbon in each molecule. The remaining atoms were found by successive factor (Busing et al., 1962) and electron density map calculations (Hubbard et al., 1971). The ring hydrogen atom on each molecule was put in at a position 1.05 Å from the corresponding ring carbon and its isotropic temperature factor was fixed at 4.5 Å². Parameters of all 32 nonhydrogen atoms were refined via a full-matrix least-squares procedure (Busing et al., 1962) minimizing the function $\sum \omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma^2 F$. This refinement converged to a conventional crystallographic residual index of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.078$. Scattering factors used were those of Hanson et al. (1960) for the nonhydrogen atoms and those of Stewart et al. (1965) for the hydrogen atoms. Final positional parameters are listed in Table I and the final thermal parameters are part of the supplementary material.

DESCRIPTION OF STRUCTURE AND DISCUSSION

Selected interatomic distances and angles (Busing et al., 1964) are listed in Tables II and III, respectively, and are in good agreement with distances and angles in previously reported insecticides, particularly those of fospirate and chlorpyrifos (Baughman and Jacobson, 1977; Baughman et al., 1978b). A view of molecule B depicting 50% probability ellipsoids (Johnson, 1971) is provided in Figure 1. Both of the molecules, A and B, can be seen in the unit cell drawing (Figure 2). The pyridoxal group is again found to be essentially planar (cf. Figure 1), the greatest deviation from the least-squares plane defined by the six-membered ring, the three attached chlorines and O(1)

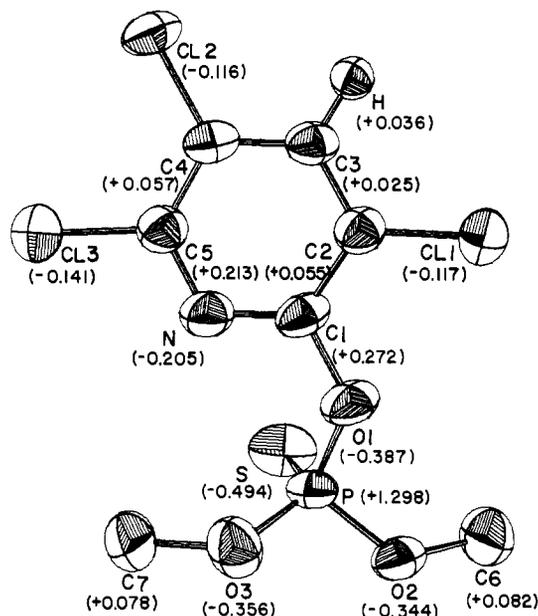


Figure 1. View of Dowco 214 molecule B with partial charge densities obtained from CNDO II molecular orbital calculations.

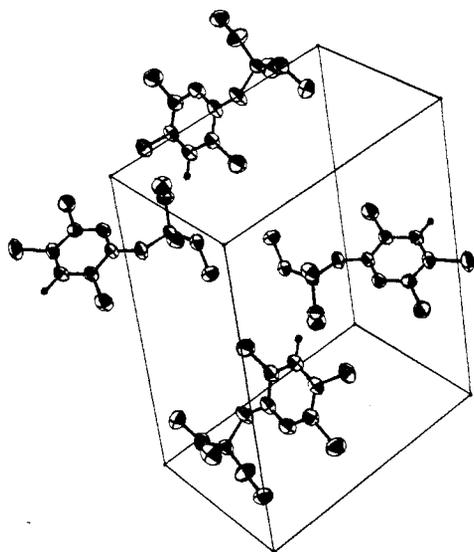


Figure 2. Unit cell of Dowco 214.

being 0.0589 Å for C1(2) (molecule A). The shortest intermolecular distance, 2.91 Å, occurs between H(2) (B) and S (A). This and other intermolecular distances indicate that the packing in the Dowco 214 crystal is primarily van der Waals in nature. This is also evident by a comparison of the distances in the two symmetry unrelated molecules in the asymmetric unit since packing environments are certainly different. Examination of these distances (Table II) show only slight variations of 4σ or less. The same is true of most of the angles with the only angles showing any appreciable deviation being those around the methoxy oxygens. This is not unexpected as there should be a very low barrier to rotation about this phosphorus-oxygen bond.

A bonding formulation involving a weak overlap of the p_z orbital on O(1) with the ring system is substantiated by the interatomic distances found and also by a CNDO II molecular orbital calculation of the Pople and Beveridge (1970) type. As in the case of previous OP insecticides whose structures have been analyzed, the C(1)-O(1) bond in Dowco 214 is significantly shorter than the other methoxy C-O bonds and also the P-O(1) bond is (by $>10\sigma$) the longest of the three P-O bonds. Thus phosphorylation

Table III. Bond Angles and Torsional Angles (deg) for Dowco 214

	Molecule A	Molecule B
Bond Angles		
S-P-O(2)	118.2 (2)	119.1 (2)
P-O(2)-C(6)	122.5 (4)	121.0 (4)
S-P-O(3)	118.5 (2)	118.2 (2)
P-O(3)-C(7)	122.0 (4)	123.8 (5)
S-P-O(1)	113.5 (2)	113.8 (2)
P-O(1)-C(1)	125.1 (3)	123.1 (4)
O(1)-P-O(2)	98.2 (2)	97.6 (2)
O(1)-P-O(3)	105.7 (2)	106.4 (3)
O(2)-P-O(3)	102.7 (2)	98.7 (3)
O(1)-C(1)-C(2)	118.0 (5)	117.8 (6)
O(1)-C(1)-N	118.5 (4)	118.9 (6)
C(1)-C(2)-C(3)	118.0 (5)	117.4 (6)
C(2)-C(3)-C(4)	119.2 (4)	119.8 (6)
C(3)-C(4)-C(5)	117.9 (5)	118.0 (5)
C(4)-C(5)-N	122.5 (5)	123.1 (6)
C(5)-N-C(1)	118.3 (5)	118.8 (5)
C(1)-C(2)-Cl(1)	120.5 (4)	121.8 (5)
C(3)-C(2)-Cl(1)	121.5 (4)	120.7 (5)
C(2)-C(3)-H	120.4 (5)	119.8 (6)
C(4)-C(3)-H	120.4 (5)	120.4 (5)
C(3)-C(4)-Cl(3)	120.1 (4)	119.8 (5)
C(5)-C(4)-Cl(3)	122.0 (5)	122.2 (5)
C(4)-C(5)-Cl(4)	121.0 (4)	120.8 (5)
N-C(5)-Cl(4)	116.5 (4)	116.0 (5)
N-C(1)-C(2)	123.5 (5)	123.3 (5)
Torsional Angles		
P-O(1)-C(1)-C(2)	-164.47	-144.66
C(1)-O(1)-P-S	50.89	48.01
C(1)-O(1)-P-O(2)	177.86	174.39
C(1)-O(1)-P-O(3)	-76.25	-84.11
S-P-O(2)-C(6)	52.17	49.41
S-P-O(3)-C(7)	177.87	-23.33

(Clark et al., 1964) should be enhanced. Dowco 214, like the other pyridoxyl OP insecticides chlorpyrifos and fospirate, displays a C(1)-O(1) bond length $\sim 4\sigma$ less than that of the phenoxy OP insecticide; this is possibly the result of replacement of a ring carbon by that of the more electronegative nitrogen.

The tetrahedral geometry about the phosphorus atom is distorted such that the S=P-O angles are greater than the O-P-O angles. Dowco 214 exhibits internal ring angles identical within standard deviations to those found for chlorpyrifos and fospirate, the angles involving nitrogen as the terminal atom being greater than 120° and all other internal ring angles being less than 120° (cf. Table III). As discussed in prior papers, the orientation of the ring group relative to the P=S (or P=O) may be a reaction variable for OP insecticide interaction with AChE. The angle between the normal to the ring and the P=S vector is 26.9° in molecule A and 16.8° in molecule B, both of which are in the range observed for the more toxic OP insecticides previously studied.

If one considers a plane that is perpendicular to the pyridoxyl ring and contains the C(1)-O(1) bond, it is seen (Figure 1) that as in the case of other insecticides (ronnel, crufomate, ronnel oxon, fospirate, and chlorpyrifos), the phosphorus atom and the Cl(1) atom are on opposite sides of this plane. The position of the phosphorus atom in Dowco 214 is apparently dictated by a barrier to rotation about the C(1)-O(1) bond caused by interactions between the phosphorus atom and Cl(1) or N. Since there is no substituent on the nitrogen atom, the thiophosphate group can to some extent rotate toward the nitrogen thus avoiding close contact with Cl(1); the P-O(1)-C(1)-C(2) torsional angle is 164.5° in molecule A and 144.7° in molecule B. The remaining torsional angles are quite similar with the exception of S-P-O(3)-C(7). The dif-

ference here amounts to almost a 180° rotation of the methyl group about the P–O(3) bond and implies some stability for either one of these positions. Since the van der Waals forces involving these molecules are different due to their different environments, one can postulate that this configuration, with C(7) in either of the positions noted above, is representative of the molecule in free space.

Organophosphorus insecticides cause autotoxicosis through inhibition of acetylcholinesterase (AChE). It has been reported that the acetylcholine molecule, in its proper configuration to interact with bovine erythrocyte AChE, has an active site separation of 4.7 Å, while fly head AChE shows an anionic-esteratic center distance of up to 5.7 Å (Hollingsworth et al., 1967). Thus, compatibility of charges at appropriate distances must be considered when choosing probable active sites on the OP insecticide. As a first approximation to the OP active sites only two atoms will be considered in accordance with Krupka's (1964) active site model of AChE (however, also see O'Brien et al., 1974). Without any further knowledge of the structure of the AChE, steric interactions around the active site can only be inferred.

The results of a CNDO II molecular orbital calculation (Pople and Beveridge, 1970) on Dowco 214 show that there are, in addition to the phosphorus, three probable positive centers that could be involved in enzyme bonding in insects (cf. Figure 1 and Tables II and III). These are C(3), C(4), and H which are respectively at 4.93, 5.14, and 5.85 Å from the phosphorus in the molecule B and 5.01, 5.18, and 5.95 Å from the phosphorus in molecule A. These are within the insect range 5.0–5.5 Å (Hollingsworth et al., 1967) and/or 4.5–5.9 Å (O'Brien, 1963) and yet outside the mammalian site separation range 4.3–4.7 Å (Hollingsworth et al., 1967; O'Brien, 1963). It may also be the case that there is a region of $\delta(+)$ charge between C(3) and its hydrogen that could also give a distance appropriate for AChE interaction. The P–C(5) distance of 4.28 Å could accommodate mammalian AChE and may help account for Dowco 214's toxic effects.

Supplementary Material Available: A listing of the final thermal parameters and the observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Received for review July 28, 1978. Accepted February 5, 1979. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division.